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Wang et al.

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(54) **HIGH-RESOLUTION
PARALLEL-DETECTION SENSOR ARRAY
USING PIEZO-PHOTOTRONICS EFFECT**

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filed on Oct. 4, 2011, now Pat. No. 8,530,983.

(60) Provisional application No. 61/590,166, filed on Jan.
24, 2012, provisional application No. 61/473,345,
filed on Apr. 8, 2011.

(51) **Int. Cl.**

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H01L 27/15 (2006.01)
H01L 21/77 (2006.01)
B82Y 10/00 (2011.01)
B82Y 15/00 (2011.01)

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(2013.01); **B82Y 15/00** (2013.01); **B82Y 20/00**

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H01L 29/84 (2013.01); **H01L 29/872**
(2013.01); **H01L 33/0008** (2013.01); **H01L**
33/18 (2013.01); **H01L 41/1132** (2013.01)

(58) **Field of Classification Search**

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USPC 257/415, 414, 417; 438/34
See application file for complete search history.

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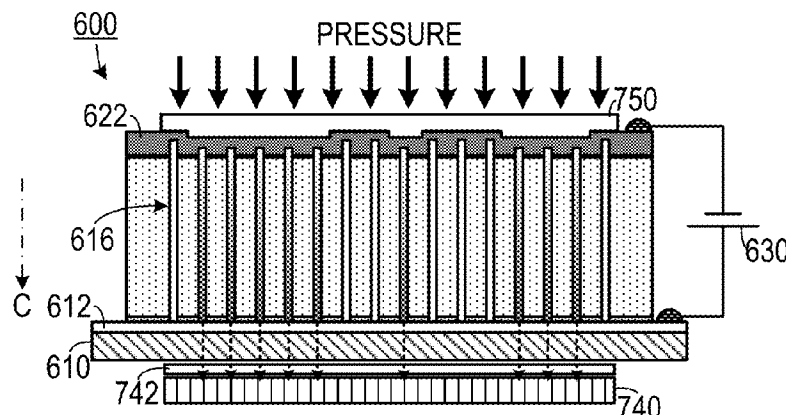
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(57)

ABSTRACT

A pressure sensor element includes a substrate, a first type of semiconductor material layer and an array of elongated light-emitting piezoelectric nanostructures extending upwardly from the first type of semiconductor material layer. A p-n junction is formed between each nanostructure and the first type semiconductor layer. An insulative resilient medium layer is infused around each of the elongated light-emitting piezoelectric nanostructures. A transparent planar electrode, disposed on the resilient medium layer, is electrically coupled to the top of each nanostructure. A voltage source is coupled to the first type of semiconductor material layer and the transparent planar electrode and applies a biasing voltage across each of the nanostructures. Each nanostructure emits light in an intensity that is proportional to an amount of compressive strain applied thereto.

16 Claims, 5 Drawing Sheets



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H01L 29/41 (2006.01)
H01L 33/00 (2010.01)
H01L 33/18 (2010.01)
G01L 1/00 (2006.01)

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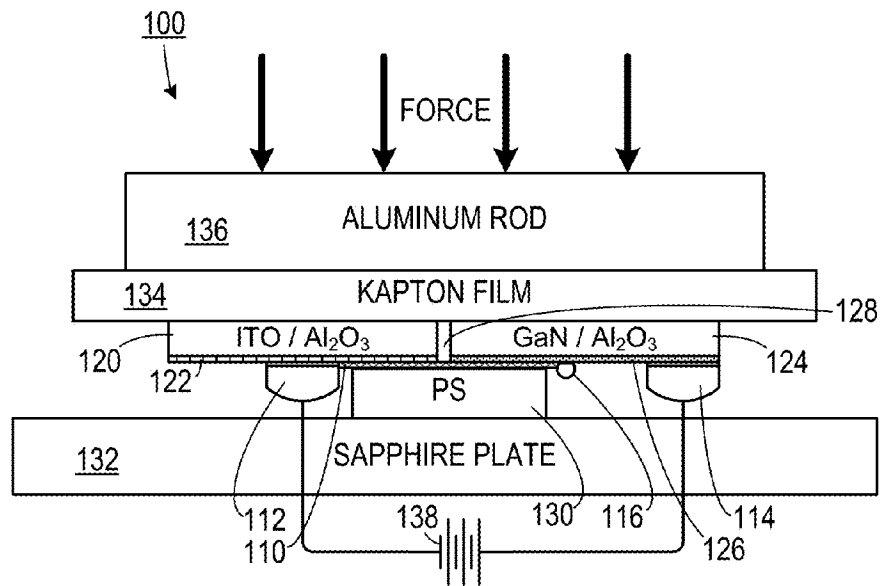


FIG. 1

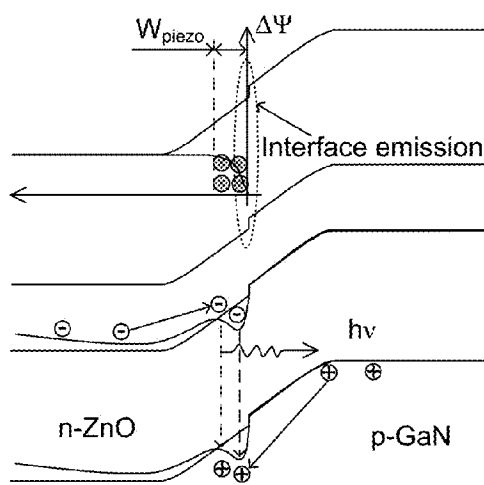


FIG. 2A

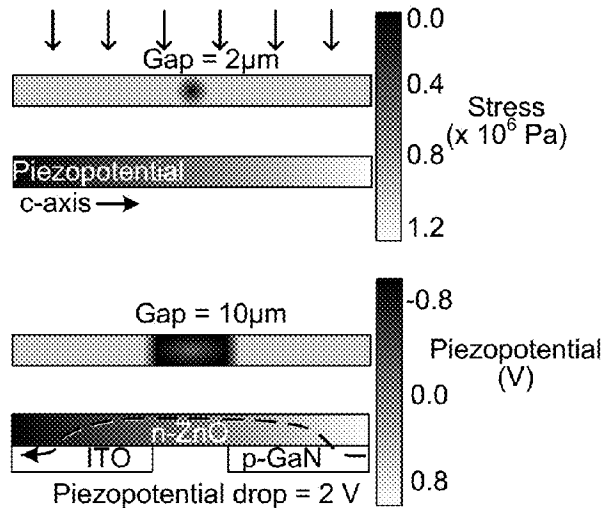


FIG. 2B

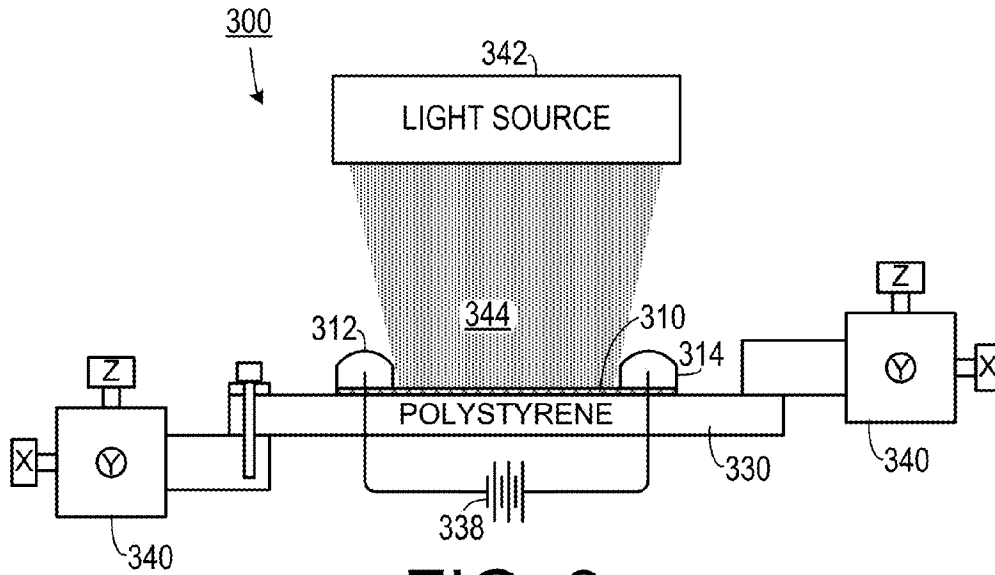


FIG. 3

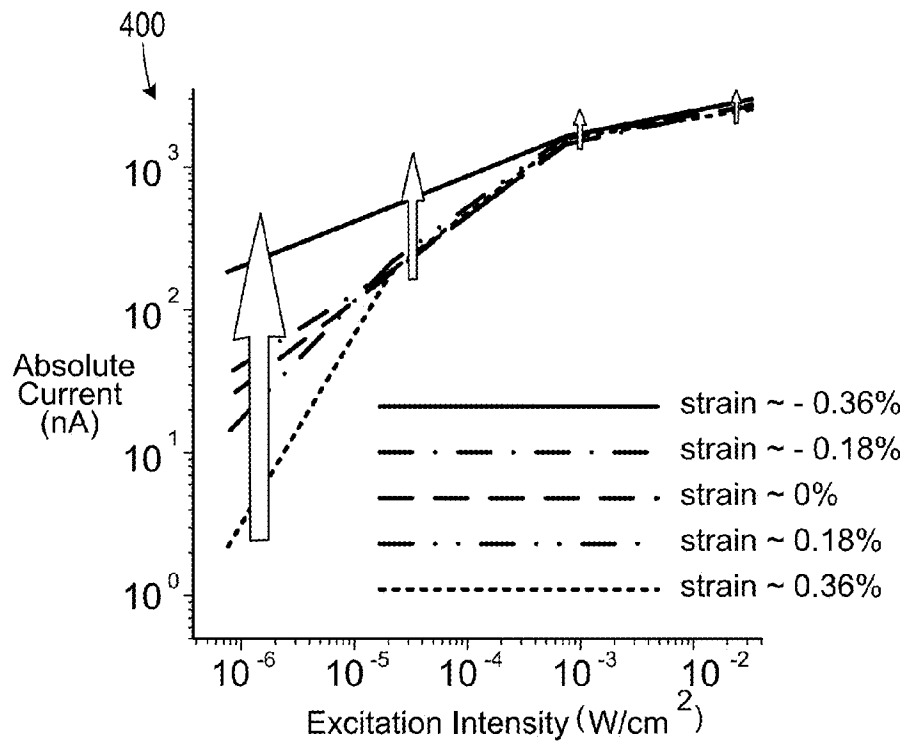


FIG. 4

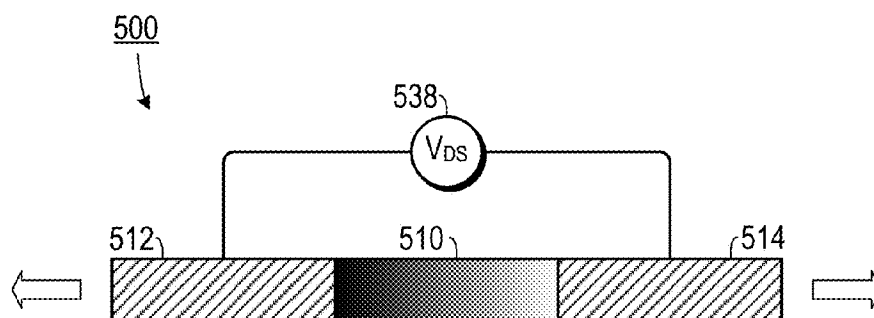


FIG. 5A

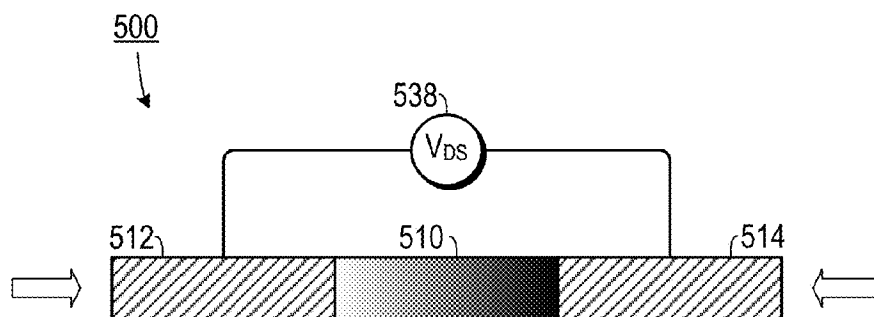


FIG. 5B

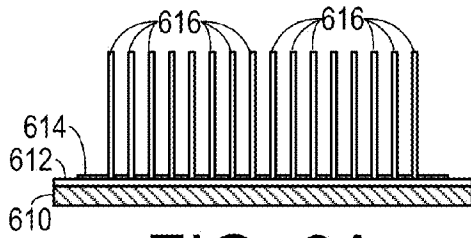


FIG. 6A

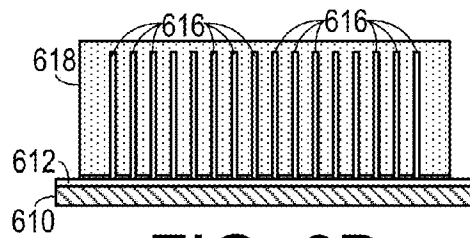


FIG. 6B

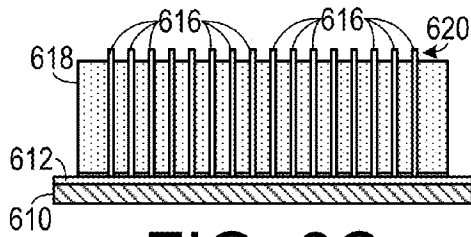


FIG. 6C

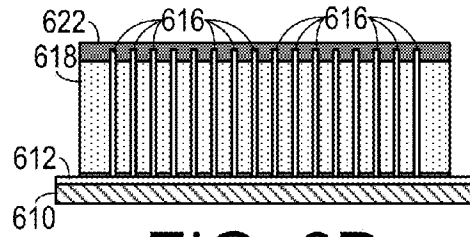


FIG. 6D

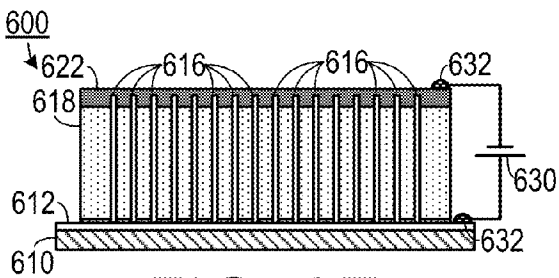


FIG. 6E

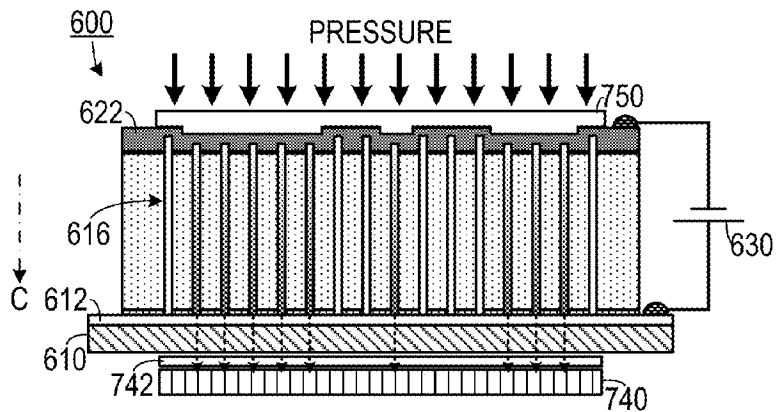


FIG. 7



FIG. 8A

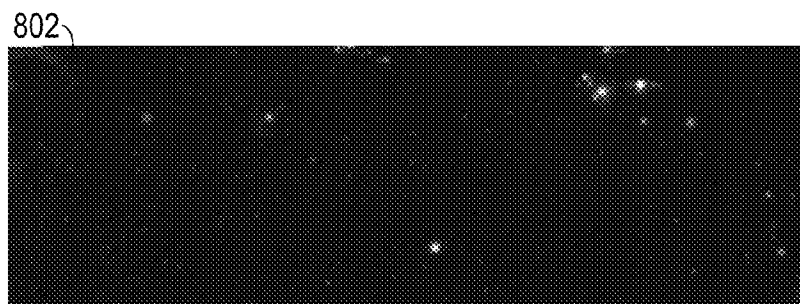


FIG. 8B

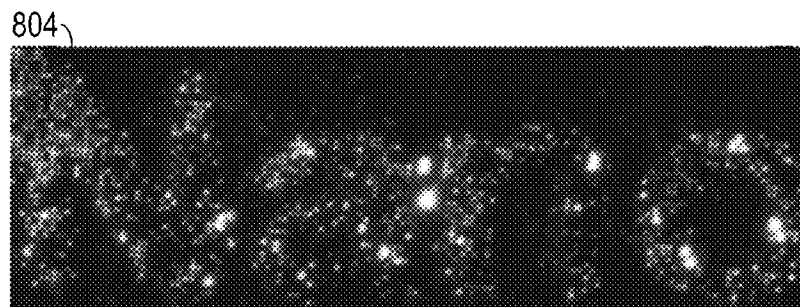


FIG. 8C

1

HIGH-RESOLUTION PARALLEL-DETECTION SENSOR ARRAY USING PIEZO-PHOTOTRONICS EFFECT

CROSS-REFERENCE TO RELATED APPLICATION(S)

This application claims the benefit of U.S. Provisional Patent Application Ser. No. 61/590,166, filed Jan. 24, 2012, the entirety of which is hereby incorporated herein by reference. This application is a continuation-in-part of and claims the benefit of U.S. Provisional patent application Ser. No. 13/252,314, filed Oct. 4, 2011, the entirety of which is hereby incorporated herein by reference.

STATEMENT OF GOVERNMENT INTEREST

This invention was made with government support under agreement No. DE-FG02-07ER46394, awarded by the Department of Energy, and under agreement No. CMMI-0946418, awarded by the National Science Foundation. The government has certain rights in the invention.

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to light emitting semiconducting devices and, more specifically, to a light emitting semiconductor device that is sensitive to pressure.

2. Description of the Related Art

Semiconductor devices are used in many different applications, including diodes, transistors, light emitting devices and sensing devices. While such semiconducting devices can be considerably more efficient than their macro-scale electrical counterparts, they still use a considerable amount of energy. Such energy usage can result in several disadvantageous phenomena, such as increased heat output and shortened battery life.

Emulation of human senses by electronic means has long been a significant challenge for robotics and other computer applications. The sense of touch is especially hard to mimic, since such emulation would require massive pressure sensor arrays that are highly sensitive, have high spatial resolution and a fast response. A touch pad is one example of a pressure sensor. However, typical touch pads lack the resolution of the nerve endings in skin by many orders of magnitude.

Several examples of pressure sensor arrays employ assembled nanowires, organic transistors or micro-structured rubber layers that sense changes in capacitance or resistance. Such systems have been mapped strain distribution in a matrix format at a resolution in the order of millimeter-scale. However, human skin has a resolution of better than 50 μm . Without such level of resolution, many sensor systems are severely limited.

Therefore, there is a need for pressure sensor arrays having high resolution.

SUMMARY OF THE INVENTION

The disadvantages of the prior art are overcome by the present invention which, in one aspect, is a pressure sensor element that includes a substrate. A first type of semiconductor material layer is disposed on the substrate. An array of elongated light-emitting piezoelectric nanostructures extends upwardly from the first type of semiconductor material layer along a selected axis. Each piezoelectric nanostructure includes a second type of semiconductor material coupled to

2

the first semiconductor material layer thereby forming a p-n junction therebetween. Each nanostructure has a bottom end electrically coupled to the first type of semiconductor material layer and a spaced apart top end. An insulative resilient medium layer is infused around each of the elongated light-emitting piezoelectric nanostructures, except for a top portion adjacent to the top end of each nanostructure, so as to provide lateral support for the nanostructures. A transparent planar electrode is disposed on the resilient medium layer and is electrically coupled to the top portion of each nanostructure. A voltage source is coupled to the first type of semiconductor material layer and the transparent planar electrode. The voltage source is configured to apply a predetermined biasing voltage across each of the nanostructures so as to cause the nanostructures to emit light. Each nanostructure is configured to emit light along the selected axis in an intensity that is proportional to an amount of compressive strain applied to each nanostructure.

In another aspect, the invention is a pressure sensor that includes: a substrate, a planar p-GaN layer disposed on the substrate and an array of elongated light-emitting piezoelectric n-zinc oxide nanowires that each extend upwardly from the p-GaN layer along a selected axis. Each nanowire has a bottom end electrically coupled to the p-GaN layer so as to form a p-n junction therebetween. Each nanowire has a top end spaced apart from the bottom end. A layer of PMMA is disposed on the planar p-GaN layer and is infused into the array of the elongated light-emitting piezoelectric zinc oxide nanowires. An ITO planar electrode is disposed on the resilient medium layer and is electrically coupled to the top portion of each nanowire. A voltage source is configured to apply a predetermined biasing voltage between the p-GaN layer and the ITO planar electrode so as to bias each of the nanowires. An array of light sensors is configured to detect light emitted by each nanowire when the nanowire is subjected to compressive strain.

In yet another aspect, the invention is a method of making a pressure sensor element, in which a planar p-GaN layer is applied to a transparent substrate. At least one elongated light-emitting piezoelectric n-semiconductor nanostructure is grown from the p-GaN layer so as to form a p-n junction between the p-GaN layer and the n-semiconductor nanostructure. A planar electrode is applied to a top portion of the elongated light-emitting piezoelectric nanostructure. A voltage source is electrically coupled to the planar p-GaN layer and to the planar electrode. The voltage source is configured to apply a predetermined biasing voltage between the first electrode and the second electrode. The biasing voltage is sufficient to cause the light-emitting piezoelectric nanostructures to emit light when subjected to compressive strain in an intensity that is proportional to an amount of compressive strain applied to each nanostructure.

These and other aspects of the invention will become apparent from the following description of the preferred embodiments taken in conjunction with the following drawings. As would be obvious to one skilled in the art, many variations and modifications of the invention may be effected without departing from the spirit and scope of the novel concepts of the disclosure.

BRIEF DESCRIPTION OF THE FIGURES OF THE DRAWINGS

FIG. 1 is a schematic diagram of a light emitting semiconducting device.

FIG. 2A is a schematic energy band diagram demonstrating band relationships in piezoelectric semiconducting devices with different amounts of strain applied thereto.

FIG. 2B is a schematic diagram demonstrating stress being applied to a piezoelectric structure and corresponding piezopotentials resulting therefrom.

FIG. 3 is a schematic diagram of a light detecting device.

FIG. 4 is a graph relating absolute current to excitation intensity detected in the device shown in FIG. 3.

FIGS. 5A-5B are schematic diagrams of piezoelectric semiconducting switching devices.

FIGS. 6A-6E are schematic diagrams showing a method of making a pressure sensor.

FIG. 7 is a schematic diagram of a pressure sensor to which pressure is applied.

FIGS. 8A-8C are micrographs showing one experimental embodiment.

DETAILED DESCRIPTION OF THE INVENTION

A preferred embodiment of the invention is now described in detail. Referring to the drawings, like numbers indicate like parts throughout the views. Unless otherwise specifically indicated in the disclosure that follows, the drawings are not necessarily drawn to scale. As used in the description herein and throughout the claims, the following terms take the meanings explicitly associated herein, unless the context clearly dictates otherwise: the meaning of “a,” “an,” and “the” includes plural reference, the meaning of “in” includes “in” and “on.”

U.S. patent application Ser. No. 12/945,077 filed Nov. 12, 2010 by Wang et al. discloses methods of making piezophotronic devices and is incorporated herein by reference.

As shown in FIG. 1, one embodiment of a piezoelectric semiconductor includes a light emitting device 100. This embodiment includes a piezoelectric structure 110 that can include, for example, ZnO, GaN, or a wurtzite structured material. In one embodiment, the piezoelectric structure 110 includes a ZnO nanowire. An ITO film 122 is deposited on an Al₂O₃ substrate 120 and a conductor 112 is placed in electrical communication with both the ITO film 122 and the piezoelectric structure 110. Another Al₂O₃ substrate 124 has an Mg-doped GaN film 126 deposited thereon. The piezoelectric structure 110 is affixed to the Mg-doped GaN film 126 by an attaching substance 116 and a conductor 114 is placed in electrical communication with the Mg-doped GaN film 126. A gap 128 is defined between the two Al₂O₃ substrates 122 and 124 and it is bridged by the piezoelectric structure 110. The two Al₂O₃ substrates 122 and 124 are affixed to a polyimide film 134 (such as Kapton). A clear rigid plate 132 (such as a sapphire plate) has a resilient pad 130 (such as a piece of polystyrene) affixed thereto. The transparent resilient layer 130 is placed against the piezoelectric structure 110. A force is applied to the polyimide film 134 by means of a metal rod 136, which causes differential bending of the piezoelectric structure 110, thereby maintaining a strain therein. When a voltage source 138 applies a potential between the electrical contacts 112 and 114, the device emits light.

In one experimental embodiment, the piezo-phototronic effect has been effectively utilized to enhance the external efficiency of an LED 100 fabricated using a single ZnO micro-/nano-wire 110 on a GaN substrate 126. The emission light intensity and injection current at a fixed applied voltage has been enhanced by a factor of 17 and 4 after applying a 0.093% compressive strain, respectively, and the corresponding conversion efficiency was improved by a factor of 4.25. This is suggested arising from an effective increase in the

local “biased voltage” as a result of the band modification caused by piezopotential and the trapping of free carriers at the interface region in a channel created by the piezopotential near the interface. Furthermore, the piezoresistance and piezooptic (photoelastic) effects have been utilized to tune the light emitting intensity, spectra and polarization simultaneously. The piezo-phototronic effect can be effectively used for enhancing the efficiency of energy conversion in today’s safe, green and renewable energy technologies.

A single ZnO micro-/nanowire LED 100 was fabricated by manipulating a ZnO wire 110 on a etched substrate. A Mg doped p-type GaN film 126 was epitaxially grown on a sapphire substrate 124 by metal organic chemical vapor deposition (MOCVD) and was used to form a p-n junction with n-type ZnO wire 110. An ITO coated 122 sapphire substrate 120 was used as the cathode that was placed side-by-side with the GaN substrate 126 with a well-controlled gap 128. The ZnO wire 110 was placed across the gap 128 with a close contact with the GaN film 126. A transparent polystyrene (PS) tape 130 was used to cover the ZnO nanowire 110. A normal force was applied on the PS film 130 by an alumina rod 136 connected to a piezo nano-positioning stage (not shown). In this case, a compressive stress was applied uniformly normal to the interface between the side surface of the ZnO wire 110 and the GaN substrate surface 126. Such a compressive force along the a-axis of the ZnO wire 110 resulted in a tensile strain along the c-axis, the growth direction of the wire 110. In this embodiment, there was no transverse bending or twist on the wire 110 to ensure the stability of the p-n junction interface between the ZnO wire 110 and GaN substrate 126.

The external efficiency of an as-fabricated single wire LED was measured conservatively to be about 1.84% before applying a strain, which is as high as that for a single p-n junction based UV LED. To test the strain effect on a single ZnO wire LED, the experiment systematically investigated its output light intensity, electroluminescence spectra and polarization as the strain being applied. At a fixed applied bias above the turn-on voltage (3 V), the current and light emission intensity increased obviously with increase of the compressive strain. The significantly enhanced light intensity was also directly observed in optical images recorded by a CCD. The injection current and output light intensity were largely enhanced by a factor of 4 and 17, respectively, after applying a 0.093% a-axis compressive strain, indicating that the conversion efficiency was improved by a factor of 4.25 in reference to that without applying strain. This means that the external true efficiency of the LED can reach about 7.82% after applying a strain.

To confirm the validity of the observed data, the stability of the contact between ZnO wire and GaN was carefully examined by repeating the applied strain. Once the strain was retracted, the light emission intensity dropped back to the value observed at strain free case. A linear relationship observed in the enhancement factor with strain proved that a possible change in contact area between n- and p-side of the device was not responsible to the observed increase in efficiency.

As shown in FIGS. 2A and 2B, when the n-ZnO wire/p-GaN substrate LED is under axial straining, two typical effects influence the output light intensity and spectra. One is the piezoresistance effect, which is caused by the change in bandgap and possibly density of states in the conduction band. This effect acts as adding a serial resistance to the LED. The second effect is the piezo-phototronic effect, which is about the tuning of the optoelectronic process at the interface using the piezopotential created along the ZnO wire. ZnO has

a non-central symmetric crystal structure, in which the cations and anions are tetrahedrally coordinated. A straining on the basic unit results in a polarization of the cations and anions, which is the cause of the piezopotential inside the crystal. As for the ZnO (n-type)-GaN (p-type) LED, a schematic diagram of its band structure is presented in FIG. 2A. Since the size of the GaN substrate is much larger than that of the ZnO microwire, the strain in GaN is much smaller than that in ZnO, thus the focus is on the piezoelectric effect from ZnO. Under an assumption of no-doping or low-doping in ZnO for simplicity, numerically calculated piezopotential distribution in the ZnO microwire, as shown in FIG. 2B, shows that a negative potential drop is created along its length when the ZnO microwire is under a-axis compressive strain. The finite doping in the wire may partially screen the piezoelectric charges, but it cannot totally eliminate the piezoelectric potential if the doping level is low, thus a dip in the band is possible. The low-doping in ZnO wire here is consistent with our experiment results because the ZnO wire is fabricated by a high-temperature thermal evaporation process using pure ZnO powders as the source. If the c-axis of the ZnO wire is pointing from the ITO side to the GaN side, as shown in FIG. 2B, the effect of the local negative piezopotential at the ITO side is equivalent to applying an extra forward biased voltage on the device. Thus, the depletion width and internal field are reduced under this additional component of forward biased voltage. Subsequently, the injection current and emitting light intensity under the same externally applied forward voltage increase when the device is strained. Alternatively, if the c-axis of the ZnO wire is reversed and pointing away from the GaN side, the GaN side has a lower piezopotential, which is equivalent to applying an extra reversely biased voltage on the device. The depletion width and internal field are thus increased, resulting in a reduction of the injection current and emitting light intensity with the increase of the applied strain.

The light output of LED is proportional to the external efficiency and injection current. Meanwhile, the injection current across the p-n junction increases exponentially with the increase of the forward bias voltage (for $V \gg kT/q$) according to the Shockley equation. Therefore, the change in light emission intensity under strain can be described by):

$$\ln\left(\frac{\Phi_{out}(\epsilon)}{\Phi_{out}(0)}\right) = \ln\left(\frac{I(\epsilon)}{I(0)}\right) + \ln\left(\frac{\eta_{ex}(\epsilon)}{\eta_{ex}(0)}\right) = \frac{\Delta\psi}{kT} + f(\epsilon)$$

where $\eta_{ex}(\epsilon)$ and $\eta_{ex}(0)$ represent the output external efficiency of LED with and without applying a strain, respectively, k is the Boltzmann constant, T is temperature, and $f(\epsilon)$ represents the effect of strain on external efficiency.

The enhancement factor for light emission was larger than that for the injection current, which means that the quantum efficiency was enhanced with the increase of strain according to the above equation. By solving Poisson equation with coupling piezoelectric effect, the enhancement of external efficiency may be caused by the localized positive piezopotential near GaN/ZnO interface, which produces carrier trapping channels (as shown in FIG. 2A). Electrons and holes can be temporarily trapped and accumulated in the channels in the conduction and valance band, respectively. Since abundant electrons are available in ZnO, for instance, the efficiency of the LED is largely dominated by the local concentration of holes because of the high activation energy of the most commonly used acceptor dopants (Mg) in GaN (~200 meV). The trapped holes may increase the hole injection from p-GaN

into n-ZnO, which increases the recombination efficiency of electrons and holes near the junction, resulting in a large increase in emission intensity. It is pointed out that, though the absolute values of the band offset varies in different reports, and is dependent on the fabrication process of the heterojunction, the band offset values do not affect the tendency of the band modification and the profile of the carrier trapping channel by piezopotential.

The peak positions of the four emission bands did not exhibit any appreciable shift under straining, but they did have obvious blue shift as the applied bias voltage was increased. The bandgap of ZnO decreases under compressive a-axis strain, while the bandgap of GaN also decreases under compressive c-axis strain. In this case, the peak position should have a red shift under compressive strain. On the other hand, the emission centers of the n-ZnO/p-GaN LED have blue shift with the increase of injection current due to the band renormalization, band filling at high current and/or the increased kinetic energies of electrons and holes. When these two complementary effects co-exist, one may balance the other, resulting in negligible shift in emission peaks. The change in refraction index of ZnO is also possible under strain, which is the photoelastic effect.

The performance of an LED is dictated by the structure of the p-n junction and the characteristics of the semiconductor materials. Once an LED is made, its efficiency is determined largely by the local charge carrier densities and the time at which the charges can remain at the vicinity of the junction. The latter is traditionally controlled by growing a quantum well or using a built-in electronic polarization for "trapping" electrons and holes in the conduction and valance bands, respectively. Instead of using this pre-fabricated structure, the piezopotential is created in ZnO by strain to control the charge transport process at the ZnO—GaN interface, demonstrating the first LED whose performance is controlled by piezoelectric effect. The emission intensity and injection current at a fixed applied voltage have been enhanced by a factor of 17 and 4 after applying a 0.093% compressive strain, respectively, and the corresponding conversion efficiency has been improved by a factor of 4.25 in reference to that without applying strain! And an external efficiency of 7.82% has been achieved. This significantly improved performance is not only attributed to the increase of injection current by the modification of the band profile, but also to the effect of the creation of a trapping channel for holes near the heterojunction interface, which greatly enhances the external efficiency. An increase in UV-to-visible ratio and stabilization of the peak position show that the spectrum quality is improved by external straining. In addition, the polarization of the output light has been modulated by the piezooptic effect. This discovery is important not only for exploring the piezo-phototronic effect through a three-way coupling among mechanical, electronic and optical properties, but also can largely improve the efficiency and performance of LEDs and the design of a large range of optoelectronic devices based on ZnO and GaN with the use of their piezoelectric property.

In another embodiment, as shown in FIG. 3, the device may be configured as a photo detector 300. An experimental version of this embodiment includes a metal-semiconductor-metal structure (MSM). The contacts 312 and 314 at the two ends of the semiconductor wire 310 are two back-to-back Schottky contacts. The device was fabricated by bonding a ZnO micro/nanowire 310 laterally on a polystyrene (PS) substrate 330, which has a thickness much larger than the diameter of the ZnO micro/nanowire 310. The mechanical behavior of the device was dominated by the substrate by considering the relative size of the wire 310 and the substrate

330. Strain was induced in the nanowire **310** by two strain-inducing structures **340** that were coupled to opposite ends of the PS substrate **330**. A bias voltage from a voltage source **338** was applied to the contacts **312** and **314**. The strain in the wire **310** was mainly axial compressive or tensile strain depending on the bending direction of the PS substrate **330**, and it was quantified by the maximum deflection of the free end of the substrate. Monochromatic UV, blue and green light **334** from a light source **342** illuminated the ZnO wire **310** to test the performance of the device. The photocurrent flowing through the nanowire **310** was a function of the intensity of the light **344** and the strain induced in the nanowire **310**.

The ZnO micro/nanowires used in one experimental embodiment were synthesized by a high-temperature thermal evaporation process. A single ZnO wire **310** was bonded on a PS substrate **330** (typical length of about 7 cm, a width of about 15 mm and thickness of 0.5 mm) with silver paste. A very thin layer of polydimethylsiloxane (PDMS) (not shown) was used to package the device, which kept the device mechanically robust under repeated manipulation and prevented the semiconductor wire from contamination or corrosion. A 3D stage **340** with movement resolution of 1 μm was used to bend the free end of the device to produce a compressive and tensile strain. Another 3D stage **340** was used to fix the sample under microscope and to keep the device in focus during the substrate bending process.

A Nikon Eclipse Ti inverted microscope system was used to monitor the sample and excite the photodetector. A Nikon Intensilight C-HGFIE lamp with a remote controller was used as the excitation source **342**. Monochromatic UV (centered at 372 nm), blue (centered at 486 nm) or green light (centered at 548 nm) was illuminated on the ZnO wire to test the performance of the device, which was focused by a 10 \times microscope objective with a 17.5 mm work distance. Monochromatic light was obtained by a filter block between the source and microscope objective. There were three sets of filter blocks which used to obtain monochromatic UV, blue and green light. The optical power density impinging on the nanowire photodetector was varied by means of neutral density filters. The illumination density was determined by a thermopile power meter (Newport 818P-001-12). I-V measurement was obtained by applying an external bias to the wire and recorded using a Keithley 487 picoammeter/voltage source in conjunction with a GPIB controller (National Instruments GPIB-USB-HS, NI 488.2). In order to compare and analyze the results, time dependent photocurrent, light intensity dependent photocurrent and photocurrent used for analyzing responsivity and strain effects were measured at a fixed applied bias of -5 V from the voltage source **338**.

As shown in FIG. 4, the photocurrent increased linearly with the optical power and showed no saturation at high power levels, offering a large dynamic range from sub- $\mu\text{W}/\text{cm}^2$ to mW/cm^2 . The total responsivity of the photodetector, \mathcal{R} , is defined as

$$\mathcal{R} = \frac{I_{ph}}{P_{ill}} = \frac{\eta_{ext} q}{h\nu} \cdot \Gamma_G \quad (1)$$

$$P_{ill} = I_{ill} \times d \times l \quad (2)$$

where \mathcal{R} is the responsivity, I_{ph} photocurrent, P_{ill} the illumination power on the photodetector, η_{ext} the external quantum efficiency, q the electronic charge, h Planck's constant, ν the frequency of the light, Γ_G the internal gain, I_{ill} the excitation power, d the diameter of the ZnO wire, l is the spacing between two electrodes. Remarkably, the calculated respon-

sivity of the device is super high, approximately $4.5 \times 10^4 \text{ A W}^{-1}$ at an intensity of $0.75 \mu\text{W}/\text{cm}^2$ of UV light illumination. The internal gain can be estimated to be 1.5×10^5 by assuming $\eta_{ext}=1$ for simplicity. The high internal gain and high responsivity is attributed to the oxygen-related hole trapping states and the shrinking of the Schottky barrier upon illumination.

This embodiment behaves as a single ZnO wire sandwiched between two back-to-back Schottky diodes. When a relatively large negative voltage was applied, the voltage drop occurred mainly at the reversely biased Schottky barrier ϕ_d at the drain side, which is denoted as $V_d \approx V$. Under reverse bias and in the dark condition, thermionic emission with barrier lowering is usually the dominant current transport mechanism at a Schottky barrier, which can be described by the thermionic-emission-diffusion theory (for $V \gg 3 kT/q \sim 77 \text{ mV}$) as:

$$j_{TED}^{dark} = SA^{**} T^2 \exp\left(-\frac{q\phi_d^{dark}}{kT}\right) \times \exp\left[\frac{\sqrt{q^7 N_D \left(V + V_{bi} - \frac{kT}{q}\right)}}{8\pi^2 \epsilon_s^3} / kT\right] \quad (3)$$

$$V_{bi} = \phi_d^{dark} - (E_C - E_F) \quad (4)$$

in which S the area of the Schottky contact, A^{**} the effective Richardson constant, T the temperature, q the unit electronic charge, k the Boltzmann constant, N_D the donor impurity density, V the applied voltage, V_{bi} the built-in potential, and ϵ_s the permittivity of ZnO.

The effect of photo illumination on semiconductor thermionic emission is to lower the energy barrier by the difference between the quasi-Fermi level with photoexcitation and the Fermi level without photoexcitation and to reduce the width of depletion layer by photon generated holes trapping in the depletion layer. The current transport mechanism with illumination can be describes as:

$$j_{TED}^{ill} = SA^{**} T^2 \exp\left(-\frac{q(\phi_d^{dark} - (E_{FN} - E_F))}{kT}\right) \times \quad (5)$$

$$\exp\left[\frac{\sqrt{q^7 N_D \left(V + V_{bi} - \frac{kT}{q}\right)}}{8\pi^2 \epsilon_s^3} / kT\right] =$$

$$SA^{**} T^2 \exp\left(-\frac{q\phi_d^{ill}}{kT}\right) \times \exp\left[\frac{\sqrt{q^7 N_D \left(V + V_{bi} - \frac{kT}{q}\right)}}{8\pi^2 \epsilon_s^3} / kT\right]$$

where E_{FN} is quasi Fermi level with illumination.

This embodiment includes a piezopotential tuned low dark-current ultrasensitive ZnO wire photodetector. The device remains low dark current characteristics while increasing the responsivity dramatically for pW level light detection by piezopotential. The derived change of barrier height with strain depends on excitation light intensity, the SBH changes faster at low light intensity than that at high light intensity. The physical mechanism is explained by considering both piezopotential effect and photon generated free charges screening effect. Three-way coupling of semiconducting, photonic and piezoelectric properties of semiconductor nanowires will allow tuning and controlling of electro-optical process by strain induced piezopotential, which is the piezophototronic effect, and it will also lead to further integration between piezoelectric devices with microelectronic and optomechanical systems.

Another embodiment, as shown in FIGS. 5A-5B, includes a switching structure **500** that behaves like a transistor. The piezotronic transistor structure **500** includes a metal **512**-nanowire **510**-metal **514** structure that is biased by a voltage source **538**. The metal portions **512** and **514** can include metals such as Au or Ag. In one embodiment, the nanowire **510** includes ZnO. The principle of the piezotronic transistor is to control the carrier transport at the M-S interface through a tuning at the local contact by creating a piezopotential at the interface region in the semiconductor by applying a strain. This structure is different from a typical MOS design, in that the externally applied gate voltage is replaced by an inner crystal potential generated by piezoelectric effect, thus, the “gate” electrode can be eliminated. This means that the piezotronic transistor needs only two leads: drain and source. Secondly, the control over channel width is replaced by a control at the interface. Since the current transported across an M-S interface is the exponential of the local barrier height at the reversely biased case, the ON and OFF ratio can be rather high due to the non-linear effect. Finally, a voltage controlled device is replaced by an external strain/stress controlled device, which is likely to have complimentary applications to CMOS devices.

The device **500** under tensile strain is shown in FIG. 5A and the device **500** under compressive strain is shown in FIG. 5B. When a ZnO nanowire device is under strain, there are two typical effects that may affect the carrier transport process. One is the piezoresistance effect because of the change in band gap, charge carrier density and possibly density of states in the conduction band of the semiconductor crystal under strain. This effect is a symmetric effect on the two end contact and has no polarity, which will not produce the function of a transistor. Piezoresistance is a common feature of any semiconductors such as Si and GaAs and is not limited to the wurtzite family. The other is the piezoelectric effect because of the polarization of ions in a crystal that has non-central symmetry, which has an asymmetric or non-symmetric effect on the local contacts at the source and drain owing to the polarity of the piezopotential. In general, the negative piezopotential side raises the barrier height at the local contact of metal n-type semiconductor, possibly changing a Ohmic contact to Schottky contact, a Schottky contact to “insulator” contact; while the positive piezopotential side lowers the local barrier height, changing a Schottky contact to an Ohmic contact. But the degree of changes in the barrier heights depends on the doping type and doping density in the nanowire. The piezoelectric charges are located at the ends of the wire, thus they directly affect the local contacts. The piezotronic effect is likely limited to the wurtzite family such as ZnO, GaN, CdS and InN. The polarity of the piezopotential can be switched by changing tensile strain to compressive strain. Thus, the device can be changed from a control at source to a control at drain simply by reversing the sign of strain applied to the device.

As shown in FIGS. 6A-6E and 7, one embodiment of a pressure sensor **600** includes a substrate **610** (such as a sapphire substrate) to which a layer **612** of a first type of semiconductor is applied. In one example, the first type of semiconductor includes p-type GaN (“p-GaN”). An array of elongated light-emitting piezoelectric nanostructures **616** extend from layer **612**. The elongated light-emitting piezoelectric nanostructures **616** include a second type of semiconductor that is different from the first type of semiconductor so that nanostructures **616** form a p-n junction where they interface with layer **612**. In one embodiment, nanostructures **616** include n-type zinc oxide (n-zinc oxide) nanowires. Other

types of materials can be used for nanostructures **616**, including: InN, ZnS, CdS, ZnSe, ZnTe.

An insulative resilient medium layer **618** is infused around each of the elongated light-emitting piezoelectric nanostructures **616** so as to provide lateral support for the nanostructures. In one example, the resilient medium layer **618** can include materials such as PMMA or benzocyclobutene.

A transparent planar electrode **622** is disposed on the resilient medium layer and is electrically coupled to the top portion of each nanostructure **618**. Examples of materials that can be used to form the transparent planar electrode **622** include: GaN, ITO, FTO, CNTs, and graphene.

A voltage source **630** is coupled to the first type of semiconductor material layer **612** and the transparent planar electrode **622**. The voltage source **630** applies a biasing voltage across each of the nanostructures **616**, which causes the nanostructures **616** to act as light emitting diodes (LEDs) and emit light. As compressive strain is applied some of the nanostructures **616**, the nanostructure **616** to which strain is applied emit light along the selected axis (such as the C axis) in an intensity that is proportional to an amount of compressive strain applied to the nanostructure.

An array of light detectors **740** is disposed adjacent to either the substrate **610** or the transparent planar electrode **622**. Each of light detector in the array **740** senses light from at least one of the elongated light-emitting piezoelectric nanostructures **616**. In one embodiment, the array of light detectors **740** includes a charge coupled device. A filter **742** may be disposed between array **740** and the substrate **610** (or the planar electrode **622**) to filter out the light of undesirable frequencies not produced as a result of compressive strain being applied to the nanostructures **616**.

When a textured surface **750** applies compressive strain to some of the nanostructures **616** (these nanostructures being represented with a darkening gradient), each nanostructure **616** emits light (represented by the broken lines pointing downward from the nanostructures **616** through the substrate **610** and the filter **742**) in proportion to the amount of compressive strain applied thereto. Those to which no compressive strain has been applied emit little light, whereas those to which more compressive strain has been applied emit more light.

This is shown in the experimental embodiment shown in FIGS. 8A-8C. As shown in FIG. 8A, a textured surface **800** (that includes the letters “NANO” in this case) was used. Light emitted **802** from a pressure sensor to which no strain has been applied is shown in FIG. 8B. Once the textured surface **800** is applied to the pressure sensor, light **804** is emitted from the nanostructures subjected to strain (which in this case spells out “NANO”).

In one method of making a pressure sensor element **100**, a planar p-GaN layer **612** is applied to a transparent substrate **610**. A mask layer **614** is applied to the p-GaN layer **612** and an array of pores is formed through the mask layer **614** using photolithographic techniques so that each pore exposes a portion of the p-GaN layer **612**. The p-GaN layer **612** and the array of pores is placed into a nutrient solution, such as 5-200 mM zinc nitride and 5-200 mM HMTA (hexamethylenetetramine), for a sufficient amount of time to grow a corresponding array elongated light-emitting piezoelectric nanostructures **616** from the p-GaN layer **612** through the array of pores. In one experimental embodiment, the p-GaN layer **612** and the array of pores remains in the nutrient solution for three hours while the nutrient solution is maintained at 60° C. to 99° C.

A resilient medium layer **618** (such as, for example, PMMA) is infused into the array of elongated light-emitting piezoelectric nanostructures **616**. A top portion of each of the

11

elongated light-emitting piezoelectric nanostructures **616** is exposed through oxygen plasma etching of the top surface of the resilient medium layer **618**. A transparent planar electrode **622** (such as ITO that is applied by sputtering) is applied to the exposed top portion of the elongated light-emitting piezo-
electric nanostructures **616**. Ni/Au contacts **632** are applied
onto the p-GaN layer **612** and the planar electrode **622** using
electron beam evaporation and then are thermally annealed at
a temperature of about 500° C. for about 5 minutes. A voltage
source **630** is electrically coupled contacts **632** and applies a
predetermined biasing voltage between the contacts **632**. A
charge coupled device **740** is placed at a location so as to be
configured to sense light emitted by individual ones of the
elongated light-emitting piezoelectric nanostructures **616**.

In one experimental embodiment, the results of which are
shown in FIG. 8, a p-type 2 μm GaN film on c plane sapphire
fabricated by metal organic chemical vapor deposition
(MOCVD) was used. On the GaN film, a 500 nm thick SU-8
(available from MICROCHEM) photoresist layer, with pat-
terned pore diameter about 800 nm and 4 μm pitch, was
prepared by photolithography (PL). Subsequently, the sub-
strate with patterned SU-8 was then put into the nutrient
solution, containing 15 mM zinc nitride (available from Alfa
Aesar) and 15 mM hexamethylenetetramine (HMTA) (avail-
able from Fluka), for nanowires (NWs) growth at 95° C. for 3
hours in an oven. ZnO NWs grew at the GaN sites exposed to
the solution, and uniformly patterned ZnO NW arrays were
hence obtained in a scale of centimeters. After the growth of
ZnO NW arrays, a 10-nm by 100-nm layers of Ni/Au were
deposited by electron beam evaporation onto the p-GaN fol-
lowed by rapid thermal annealing in air at 500° C. for 5
minutes. After that, a relatively thick layer of PMMA (avail-
able from MICROCHEM) was spun coated to wrap around
the ZnO NWs. Then oxygen plasma was applied to etch away
the top part of the PMMA, exposing the tips of the NWs.
Then, a 100-300 nm ITO film was sputtered as the top com-
mon electrode of the entire NWs.

The above described embodiments, while including the
preferred embodiment and the best mode of the invention
known to the inventor at the time of filing, are given as
illustrative examples only. It will be readily appreciated that
many deviations may be made from the specific embodiments
disclosed in this specification without departing from the
spirit and scope of the invention. Accordingly, the scope of the
invention is to be determined by the claims below rather than
being limited to the specifically described embodiments
above.

What is claimed is:

1. A pressure sensor element, comprising:
 - (a) a substrate;
 - (b) a first type of semiconductor material layer disposed on the substrate;
 - (c) an array of elongated light-emitting piezoelectric nanostructures extending upwardly from the first type of semiconductor material layer along a selected axis, each piezoelectric nanostructure including a second type of semiconductor material coupled to the first semiconductor material layer thereby forming a p-n junction therebetween, each nanostructure having a bottom end electrically coupled to the first type of semiconductor material layer and a spaced apart top end;
 - (d) an insulative resilient medium layer infused around each of the elongated light-emitting piezoelectric nanostructures except for a top portion adjacent to the top end of each nanostructure so as to provide lateral support for the nanostructures;

12

- (e) a transparent planar electrode disposed on the resilient medium layer and electrically coupled to the top portion of each nanostructure; and
- (f) a voltage source coupled to the first type of semiconductor material layer and the transparent planar electrode and configured to apply a predetermined biasing voltage across each of the nanostructures so as to cause the nanostructures to emit light, wherein each nanostructure is configured to emit light along the selected axis in an intensity that is proportional to an amount of compressive strain applied to each nanostructure.

2. The pressure sensor element of claim 1, the transparent planar electrode each comprise a material selected from a group of materials consisting of: GaN, ITO, FTO, CNT, graphene and combinations thereof.

3. The pressure sensor element of claim 1, wherein:

- (a) the first type of semiconductor material includes an p-type semiconductor; and
- (b) the second type of semiconductor material includes an n-type semiconductor.

4. The pressure sensor element of claim 3, wherein the p-type semiconductor comprises GaN and wherein the n-type semiconductor comprises a nanowire that comprises a material selected from a group of materials consisting of: InN, ZnS, CdS, ZnSe, ZnO, ZnTe and combinations thereof.

5. The pressure sensor element of claim 1, wherein the resilient medium layer comprises a material selected from a group of materials consisting of: PMMA, benzocyclobutene and combinations thereof.

6. The pressure sensor element of claim 1, wherein the substrate comprises sapphire.

7. The pressure sensor element of claim 1, further comprising an array of light detectors disposed adjacent to a selected one of the substrate and the transparent planar electrode, each of the light detectors configured to sense light from at least one selected one of the elongated light-emitting piezoelectric nanostructures.

8. The pressure sensor element of claim 7, wherein the array of light detectors comprises a charge coupled device.

9. A pressure sensor, comprising:

- (a) a substrate;
- (b) a planar p-GaN layer disposed on the substrate;
- (c) an array of elongated light-emitting piezoelectric n-zinc oxide nanowires each extending upwardly from the p-GaN layer along a selected axis, each having a bottom end electrically coupled to the p-GaN layer so as to form a p-n junction therebetween, each nanowire having a top end spaced apart from the bottom end;
- (d) a layer of PMMA disposed on the planar p-GaN layer and infused into the array of the elongated light-emitting piezoelectric zinc oxide nanowires;
- (e) an ITO planar electrode disposed on the layer of PMMA and electrically coupled to the top portion of each nanowire;
- (f) a voltage source configured to apply a predetermined biasing voltage between the p-GaN layer and the ITO planar electrode so as to bias each of the nanowires; and
- (g) an array of light sensors configured to detect light emitted by each nanowire when the nanowire is subjected to compressive strain.

10. A pressure sensor device, comprising:

- (a) a substrate;
- (b) a first type of semiconductor material layer disposed on the substrate;
- (c) an array of elongated light-emitting piezoelectric nanostructures extending upwardly from the first type of

13

- semiconductor material layer along a selected axis, each piezoelectric nanostructure including a second type of semiconductor material coupled to the first semiconductor material layer thereby forming a p-n junction therebetween, each nanostructure having a bottom end electrically coupled to the first type of semiconductor material layer and a spaced apart top end;
- (d) an insulative resilient medium layer infused around each of the elongated light-emitting piezoelectric nanostructures except for a top portion adjacent to the top end of each nanostructure so as to provide lateral support for the nanostructures;
- (e) a transparent planar electrode disposed on the resilient medium layer and electrically coupled to the top portion of each nanostructure;
- (f) a voltage source coupled to the first type of semiconductor material layer and the transparent planar electrode and configured to apply a predetermined biasing voltage across each of the nanostructures so as to cause the nanostructures to emit light, wherein each nanostructure is configured to emit light along the selected axis in an intensity that is proportional to an amount of compressive strain applied to each nanostructure; and
- (g) an array of light detectors disposed adjacent to a selected one of the substrate and the transparent planar electrode, each of the light detectors configured to sense

14

light from at least one selected one of the elongated light-emitting piezoelectric nanostructures.

11. The pressure sensor device of claim 10, the transparent planar electrode each comprise a material selected from a group of materials consisting of: GaN, ITO, FTO, CNT, graphene and combinations thereof.

12. The pressure sensor device of claim 10, wherein the first type of semiconductor material includes an p-type semiconductor; and the second type of semiconductor material includes an n-type semiconductor.

13. The pressure sensor device of claim 12, wherein the p-type semiconductor comprises GaN and wherein the n-type semiconductor comprises a nanowire that comprises a material selected from a group of materials consisting of: InN, ZnS, CdS, ZnSe, ZnO, ZnTe and combinations thereof.

14. The pressure sensor device of claim 10, wherein the resilient medium layer comprises a material selected from a group of materials consisting of: PMMA, benzocyclobutene and combinations thereof.

15. The pressure sensor device of claim 10, wherein the substrate comprises sapphire.

16. The pressure sensor device of claim 10, wherein the array of light detectors comprises a charge coupled device.

* * * * *